REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
September 2006	Final Report	01 June 2002 - 30 June 2006

4. TITLE AND SUBTITLE
Chemical Behavior Under Extreme Conditions

5a. CONTRACT NUMBER

5b. GRANT NUMBER
F49620-02-1-0313

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Professor James L. Kinsey

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rice University
Houston TX

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
USAF/AFRL
AFOSR
875 North Randolph Street
Arlington VA 22203
Dr Michael Berman/NL

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A: Approved for public release. Distribution is unlimited

AFRL-SR-AR-TR-06-0440

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The work continues along the lines described in detail in the grant application submitted at AFOSR. This bas three main aspects: examining and understanding new phenomena, the role of electronic excistation and the more detailed examination of aspects that are broadly understood but deserve a second look. The technical report below describes a particular example of the third aspect. This has to do with the role of the extreme compression that can be achieved during cluster impact. The point of the detailed examination is to establish that prior to the expansion of the cluster there is indeed a compression stage.
The work continues along the lines described in detail in the grant application. Several papers have been submitted/published since the previous report.
The work continues along the lines described in detail in the grant application. Several papers have been submitted/ published since the previous report. A complete list is included below. As written in the earlier report, scientists from Air Force laboratories emphasize that for a variety of aerospace related applications it is necessary to better understand light emission from both natural and human-induced perturbations of the atmosphere.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(Include area code)*
U	U	U	UU	11	

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Chemical Behavior Under Extreme Conditions

AFOSR GRANT No. F49620-02-1-0313

Final Performance Report

By

James L. Kinsey and Raphael D. Levine

Rice University, Houston, Texas

Program Manager: Dr. Michael R. Berman

September, 2006

Executive summary

The physicochemical properties including energy acquisition, storage and disposal of small ultrahot and superdense clusters has been studied both theoretically and computationally. The study is primarily directed at the understanding of matter under extreme conditions, which is characteristic of many situations of direct interest to the Air Force. In addition the work has developed new computational procedures and also new insights on the cooling mechanisms, with special emphasis on light emission, of hot matter.

The extreme deviation from ambient conditions is achieved by impacting a cold cluster moving at a hypersonic speed at a hard surface. The work explored the physical changes such as the ultrafast rise in pressure of the cluster.

Experiments have already verified many of the reported new features. Work is currently in progress on observing emission from hot water clusters.

In addition to the PI's, graduate student Ms. Ayelet Gross (who will shortly get her PhD) and Dr. Mrs. Haya Kornweitz actively participated in the work. All their work is published or submitted for publication.

One new aspect to emerge from the work is that in a hot system time moves much faster. We are in the process of developing further understanding of ultrashort time processes.

Complete list of reviewed publications submitted and/or accepted during the period of this proposal

Papers acknowledging AFOSR support are indicated by an **X**

Logic Gates Using High Rydberg States,
F. Remacle , E.W. Schlag, H. Selzle, K.L. Kompa U. Even and R.D. Levine, Proc. Nat'l. Acad. Sci. US 98: 2973-2978 (2001).

IR-UV Double-Resonance Photodissociation of Nitric Acid ($HONO_2$) Viewed as Molecular Information Processing,
Th. Witte, Ch. Bucher, F. Remacle, D. Proch, K.L. Kompa and R.D. Levine, Angew. Chemie . 40, 2512 (2001).

Towards Molecular Logic Machines,
F. Remacle and R.D. Levine, J. Chem. Phys. 114, 10239-10246 (2001).

Intermolecular and Intramolecular Logic Gates,
F. Remacle, S. Speiser and R.D. Levine, J. Phys. Chem. A 105, 5589-5591 (2001).

On the Crossing of Electronic Energy Levels of Diatomic Molecules in the Large-D Limit,
Q. Shi, S. Kais, F. Remacle and R. D. Levine, J. Chem. Phys. 114, 9697-9705 (2001).

On the Capture Cross-Section for Charge Neutralization, Recombination, Photoassociation and Other Barrierless Reactions,
R.D. Levine, Chem. Phys. 270, 129-132 (2001).

Intermolecular and Intramolecular Logic Gates,
F. Remacle, S. Speiser and R.D. Levine, J. Phys. Chem. A 105, 5589-5591 (2001).

On the Crossing of Electronic Energy Levels of Diatomic Molecules in the Large-D Limit,
Q. Shi, S. Kais, F. Remacle and R. D. Levine, J. Chem. Phys. 114, 9697-9705 (2001).

Excitation of Rydberg Series in C_{60},
M. Boyle, K. Hoffmann, C.P. Schulz, I.V. Hertel, R.D. Levine and E.E.B. Campbell, Phys Rev, Lett. 87, 273401-1 - 273401-4 (2001)

Conducting Arrays of Metallic Quantum Dots: An Experimental and Computational Study of the Role of Disorder as Probed by the Surface Potential
J. L. Sample, P. Chandhar, K. C. Beverly, F. Remacle , J. R. Heath and R. D. Levine, Adv. Materials 114, 124-128 (2002)

On Spectroscopy, Control and Molecular Information Processing,
Dan Steinitz, F. Remacle and R. D. Levine, Chem. Phys. Chem. 3, 43-51 (2002)

Quantum Dot Artificial Solids: Understanding the Static and Dynamic Role of Size and Packing Disorder,
K. C. Beverly, J. L. Sample, J. F. Sampaio, F. Remacle , J. R. Heath and R. D. Levine, Proc. Natl Acad Sci US 99, 6456-6459 (2002)

Molecular Logic Machines by Optical Spectroscopy and Charge Migration Along a Molecular Wire Realized as a Peptide,
F. Remacle, R. Weinkauf, Dan Steinitz, K. L. Kompa and R. D. Levine, Chem. Phys. 282, 363-372 (2002)

Real-space renormalization group study of the Hubbard model on a non-bipartite lattice,
J. X. Wang and Sabre Kais and R.D. Levine, Intl. J. Mol. Sci. 3, 4-16 (2002).

Conductivity of 2-D Ag Quantum Dot Arrays: Computational Study of the Role of Size and Packing Disorder at Low Temperatures,
F. Remacle, K. C. Beverly, J. R. Heath and R. D. Levine, J. Phys. Chem. B 106 ,4116-4126 (2002).

X Progress in Experimental and Theoretical Studies of Clusters,
R. S. Berry and R. D. Levine,

Ultrashort Time Resolution From Energy Dependent Interference of Photodissociation Amplitudes
Elva A. Torres, Delroy Baugh and R. D. Levine, Chem. Phys. Letters, 375, 141-148 (2003)

X Driving High Threshold Chemical Reactions During the Compression Interlude in Cluster Surface Impact
A. Gross , H. Kornweitz, T. Raz, and R. D. Levine, Chem. Phys. Letters, 354, 395-402 (2002)

Size effects in the electronic properties of finite arrays of exchange coupled quantum dots: A renormalization group approach,
J. X. Wang, Sabre Kais F. Remacle and R.D. Levine, J. Phys. Chem. B 106, 12847-12850 (2002)

X Cluster-cluster Fusion
E. E. B. Campbell, A.V. Glotov, A. Lassesson and R. D. Levine, Comptes rendus de l'Académie des Sciences. série II. Physique, 3, 341-352 (2002)

Voltage-Induced Non-Linear Characteristics of Arrays of Metallic Quantum Dots,
F. Remacle and R. D. Levine , Nanoletters, 2, 697-701 (2002)

Improved corresponding states scaling of the equations of state of simple fluids,
D. Ben-Amotz, A. D. Gift, R. D. Levine, J. Chem. Phys. 117, 4632-4634 (2002)

X Dynamics of Delayed Ionization,
E.E.B. Campbell and R. D. Levine, *in* "Quantum Phenomena in Clusters and Nanostructures", S.N. Khanna and A.W. Castleman, Jr., eds. (2003).

Corresponding states,
D. Ben-Amotz, A. D. Gift, and R. D. Levine, J. Chem. Ed. 81, 142 (2004).

Voltage-Induced Phase Transition in Arrays of Metallic Nano Dots in Computed Transport and Surface Potential Structure,
F. Remacle and R. D. Levine, Appl. Phys. Letters 82, 4543-4545 (2003).

Electronic and Electrical Response of Arrays of Metallic Quantum Dots, F. Remacle and R. D. Levine, , Int. J. Quant. Chem. 99, 743-751 (2004).

Current-Voltage-Temperature Characteristics for 2D Arrays of Metallic Quantum Dots,
F. Remacle and R. D. Levine, Is. J. Chem. 42, 269-280 (2003).

X Spectroscopic Characterization of Collision-Induced Electronic Deformation Energy using Sum Rules, A. Gross and R. D. Levine, J. Chem. Phys. 119, 4283-4293 (2003).

Gating the Conductivity of Arrays of Metallic Quantum Dots,
F. Remacle, K. C. Beverly, J. R. Heath and R. D. Levine, J. Phys. Chem. B, 107, 13892-13901 (2003).

Electronic and Transport Properties of Arrays of Metallic Quantum Dots: A Computational Study,
F. Remacle and R. D. Levine, Chimie Nouvelle, 83, 112-119 (2003).

X Collision-induced IR emission spectra of impact heated clusters,
A. Gross and R. D. Levine, J. Phys. Chem. A, 107, 9567-9574 (2003)

Electrical Transmission of Molecular Bridges,
F. Remacle and R. D. Levine, Chem. Phys. Letts, 383, 537-543 (2004).

Nanowiring by Molecules,
F. Remacle, I. Willner and R. D. Levine, J. Phys. Chem. B., 108, 18129-18134. (2004).

Conductance Spectroscopy of Low Lying Electronic States of Arrays of Metallic Quantum Dots: A Computational Study,
F. Remacle and R. D. Levine, in Nanoassemblies and Superstructures, N. Kotov Ed , Marcel Dekker New York (2005),

Level crossing conductance spectroscopy of molecular bridges,
F. Remacle and R. D. Levine, Appl. Phys. Lett. 85, 1725 (2004).

X Systematics of Collision-Induced Light Emission from Hot Matter,

A. Gross Mikael Kjellberg and R. D. Levine, J. Phys. Chem. A 108, 8949-8953 (2004).

Quasiclassical Computations,
F. Remacle and R. D. Levine, PNAS 101, 12091-12095 (2004).

Electrical Addressing of Confined Quantum Systems for Quasiclassical Computation and Finite State Logic Machines
F. Remacle, J. R. Heath and R. D. Levine Proc. Natl. Acad. Sci. USA, 102, 5653-5658 (2005).

A Counter by the Electrical Input/Output Stimuli Activation of an Array of Quantum Dots
F. Remacle, I. Willner and R. D. Levine , Chem. Phys. Chem. 6, 1239-1242 (2005).

X Probing Electronic Rearrangement During Chemical Reactions
H. Kornweitz, A. Gross, G. Birnbaum and R. D. Levine, Physica Scripta, 73, C1-C5 (2006).

Molecule-Based Photonically Switched Half-Adder and the Concatenation of MolecularLogic Units by Intramolecular Transfer of Energy or of Charge,
F. Remacle, R. Weinkauf and R. D. Levine, 110, 177-184 (2006).

Temperature Dependent and Friction Controlled Electrochemically-Induced Shuttling Along Molecular Strings Associated with Electrodes,
Eugenii Katz, Ronan Baron, Itamar Willner, Noa Richke and R. D. Levine , ChemPhysChem. 6, 2179-2189 (2005).

Electrical transport in saturated and conjugated molecular wires,
F. Remacle and R. D. Levine , Faraday Discussions, 131, 45-67 (2006).

The Changing Landscape of Physical Chemistry at the Beginning of the 21st Century,
G. A. Somorjai and R. D. Levine, J. Phys. Chem. 109, 9853 (2005)

All Optical Digital Logic: Full Addition or Subtraction on a Three-State System,
F. Remacle and R. D. Levine , Phys Rev A 73, 033820 (2006).

Towards Parallel Computing: Physical Realization of a Linear Finite State Logic Machine by a Markovian Stochastic Process,
F. Remacle and R. D. Levine, submitted

X Characterization of Evanescent High Pressure During Hypersonic Cluster-Surface Impact by the Virial Theorem, A. Gross and R. D. Levine, J. Chem. Phys. 129, 194307 (2005).

Dissociation Kinetics of Peptide Ions, E. W. Schlag, H. L. Selzle, P. Schanen and R. D. Levine, J. Phys. Chem. A 110, 8497 (2006).

An Electronic Time Scale in Chemistry, F. Remacle and R. D. Levine, Proc. Natl. Acad. Sci. USA, 103, 6793 (2006).

Time Resolved Spectroscopy of Charge Migration in Molecular Wires: Computational Evidence for Rich Electronic Dynamics,
F. Remacle and R. D. Levine, J. Phys. Chem. submitted

The Time Scale for Electronic Reorganization Upon Sudden Ionization of the Water Dimer and Water-Methanol Bimer,
F. Remacle and R. D. Levine , J. Chem. Phys. Accepted

X A Mechanical Representation of Entropy of a Large Finite System,
A. Gross and R. D. Levine, J. Chem. Phys., accepted (2006).

Inter- and intramolecular level logic devices,
F. Remacle and R. D. Levine in Information Technology, R. Waser ed. (2006).

X Transitory Ultra-High Pressure During Cluster-Surface Impact,
A. Gross and R. D. Levine, Submitted

X The Entropy of a Single Large Finite System Undergoing Both Heat and Work Transfer,
A. Gross and R. D. Levine, Mol. Phys. submitted (2006).

X Book: Molecular Reaction Dynamics, Cambridge University Press 2005

Edited Special issue: In honor of the Wolf Prize to Richard N. Zare

7. Interactions/Transitions:

The work carried out under the auspices of this proposal has been reported at numerous conferences and seminars, most recently as an invited talk by Ms. Gross at the 2006 National Meeting of the American Chemical Society and as another invited talk by R. D. Levine at the first GRI meeting: Breakthrough Advances in Cluster Science. The abstract of the talk by Levine is attached as an appendix.

Levine has twice visited the Hanscom AFB to talk about systems under extreme conditions. (Fall of 2001 and summer of 2004). PowerPoint presentations of his talks are available upon request.

8. New discoveries, inventions, or patent disclosures. (If none, report None.)

None

9. Honors/Awards: List honors and awards received during the grant/contract period

In October 2002 R D Levine received the EMET Prize in the presence of J L Kinsey and R N Zare. Two one-day symposia were held on that occasion.

In September 2004 R D Levine received the MOLEC 2004 award* at the MOLEC (MOLEcular Collisions) conference in Holland.

The web based instructions for the report tell that lifetime achievement honors should be listed also prior to the present effort. I am not sure if I am to take this literally or not. Here goes **Member**: Academia Europaea (Foreign Member); American Academy of Arts and Sciences (Foreign Honorary Member); American Philosophical Society; International Academy of Quantum Molecular Science; Israel Academy of Sciences and Humanities; Max-Planck-Gesellschaft (Foreign Member, Quantum Optics); National Academy of Sciences of the United States of America (Foreign Associate); Royal Danish Academy of Sciences and Letters (Foreign Member). **Awards**: Israel Prize (Exact Sciences), 1974; Weizmann Prize, 1979; Wolf Prize, Chemistry 1988; Docteur *honoris causa*, Liege University, 1991; Rothschild Prize, Chemistry, 1992; Doctor *honoris causa*, Technische Universität München, 1996; Max Planck Prize for International Cooperation, 1996.

---

* The citation reads 'In honor of his outstanding studies of, and pioneering contributions to The Dynamics of Chemical Reactions'.

Appendix: abstract for GRI Symposium I on Breakthrough Advances in Cluster Science

Chemical, Mechanical and Radiative Cooling Processes: The Thermodynamics of Ultrahot and Dense Clusters

R. D. Levine

A cold atomic cluster can be very rapidly heated and compressed by a hypersonic impact at a hard surface. Experiments at the Cluster Research Laboratory of the Toyota Technological Institute and elsewhere have explored this novel regime of dynamics where the duration of collisions within the cluster is so short. Reviews of experimental [1] and theoretical [2] work are available.

Cluster impact can be simulated by computing a classical trajectory for the motion of the atoms in the clusters. This trajectory is mechanically reversible. In this work we discuss why the small cluster behaves like a macroscopic system and how to compute thermodynamic variables from the mechanical simulation using a single trajectory. In particular we compute the entropy of the cluster following the impact, figure 1

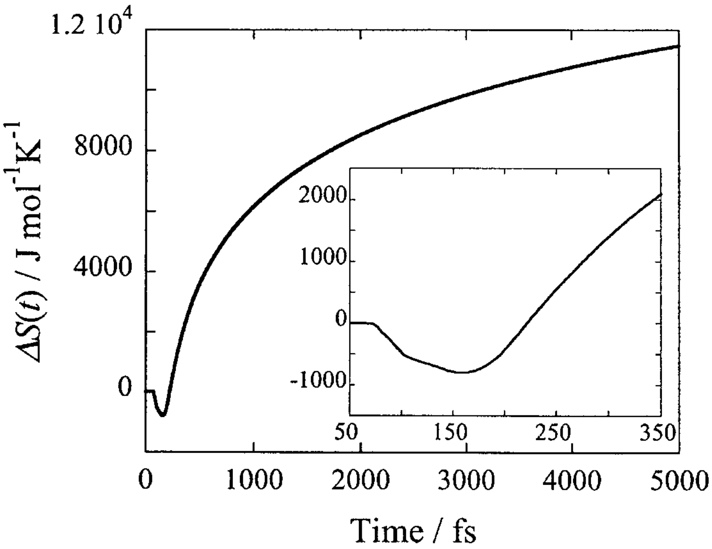
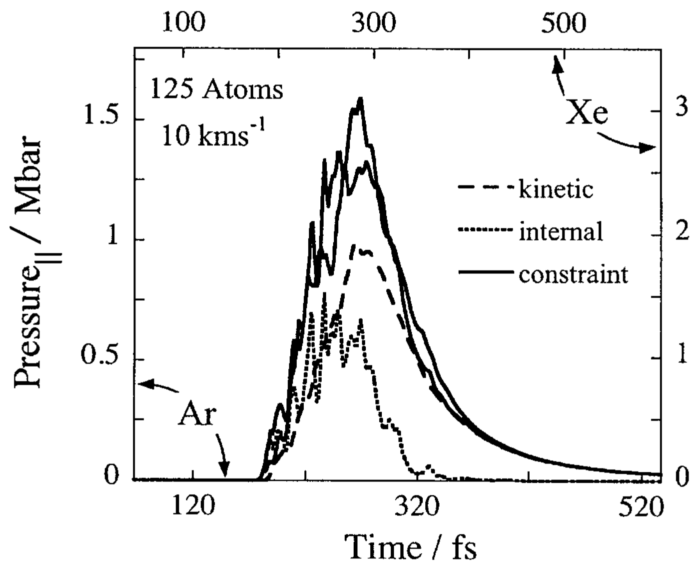


Figure 1. The increase in entropy of a cluster of 125 Ar atoms vs. time in fs. $\Delta S(t)$ is the difference between the current value of the entropy and its value for the cold cluster before the impact at 10 kms^{-1} As shown in the insert, immediately after the impact the entropy of the cluster decreases because of the compression of the cluster by the impact at the surface. From Gross, A; Levine R.D. J. Chem Phys in press

An essential ingredient in evaluating the entropy is the computation of the pressure. This required a new version of the virial theorem where the mechanical evolution of the cluster is constrained. The details have been published [3]. Here we just draw attention to the rather high pressures within the compressed clusters, figure 2. Furthermore, as shown in the figure, in the new dynamical regime the scaling of the pressure is not like the familiar law of corresponding states.



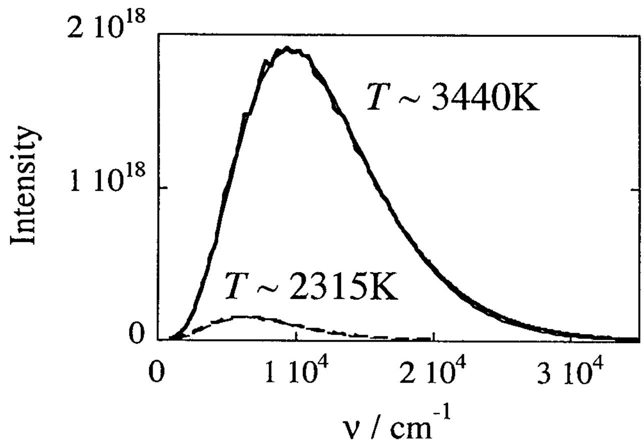


Figure 2. The pressure component in the direction parallel to the surface, solid line, in Mbar units, exerted by a cluster of 125 Ar atoms, left ordinate, or 125 Xe atoms, right ordinate vs. time in fs. The simulations are for impact velocity of 10 kms^{-1} in a direction normal to the surface. The scale of the two ordinates is in the ratio of 1.94/1. The pressure is computed from the virial theorem as a sum of two components shown, for Xe, as dashed and dotted curves.

Figure 3. Emission spectrum of a hot cluster. The temperature is that of the electrons.

Radiative cooling occurs due to the transient dipole moment of the compressed clsuter. Here too, due to the short time scale the dipole is very rapidly varying leading to emission all the way to the visible. The thermodynamic analysis of the spectrum has been published [4] and is shown in figure 3. The smooth line through the computation is the theory for a given mean kinetic energy of the electrons (expressed as a temperature).

This work was supported by the US Air Force Office of Scientific Research

References:

[1] Yasumatsu, H.; Kondow, T. *Rep. Prog. Phys.* **2003**, *66*, 1783.
[2] Raz, T.; Levine, R. D. in *Atomic and Molecular Beams*, edited by R. Campargue (Springer, Berlin, 2000).
[3] Gross, A.; Levine, R. D. *J. Chem. Phys.* **123**, 194307 (2005).
[4] Gross, A.; Levine, R. D. *J. Chem. Phys.* **119,** 4283 (2003).